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Analysis of concentrations of selected phthalic acid esters in aquatic ecosystems – Poland's case study

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ABSTRACT

This paper reviews the literature on the properties and occurrence of phthalic acid esters (phthalates) in various components of the environment. It also addresses the issue of the presence of this group's most commonly-occurring substance - di(2-ethylhexyl) phthalate (DEHP) – in Polish surface waters and their bottom sediments. Phthalates are ingredients of many such everyday objects as plastics, cosmetics, paints, and varnishes. They exhibit a high level of durability and thermal and chemical resistance, and this stability ensures the regular detection of phthalic acid esters in the environment. Unfortunately, these are also compounds capable of affecting human health adversely, impacting on the endocrine system, and also proving carcinogenic, mutagenic and teratogenic. Phthalates in general, and DEHP in particular, tend to accumulate on solid particles, as evidenced by higher contents in bottom sediments than in the aqueous phase. In Poland, contents of DEHP in bottom sediments even reach 7,100 μg/kg DW while – at 3.22 μg/L – the content noted in some surface waters may be 2.5 times the permitted level. In that context, a further aim of this paper has been to analyze possible sources of contamination of surface waters with this substance, in a region where cases of non-compliant exceedance were to be noted.

Keywords: Phthalates; Di(2-ethylhexyl) phthalate; Surface waters; Bottom sediments

1. Physicochemical characteristics and applications of phthalates

Phthalates (or phthalic acid esters) are esters of phthalic acid obtained synthetically through the esterification of phthalic acid with various alcohols [1]. The chemical structure is as depicted in Fig. 1.

At room temperature, phthalates are mostly colorless or pale yellow, oily, odorless liquids. This reflects typically-low melting points below –25°C (though diethyl phthalate (DEP) melts at +5.5°C and di-n-undecyl phthalate at –9°C) [2]. Boiling points are high, however (in the 230°C–486°C) [3]. Phthalates containing long alcohol chains have hydrophobic properties and are slightly soluble in water. In general, a chemical compound's structure affects its biodegradation, potential to undergo bioaccumulation and distribution in the environment. In that light, Table 1 presents the selected physicochemical properties of the phthalates used commonly in industry. At the most general level, the phthalates can be divided into the small-molecule and macromolecular substances. Beyond that, the molar mass of phthalic acid esters depends on the length of the alkyl chains in the molecule.

The low-molecular-weight phthalates are used in cosmetics, such as moisturizing balms, nail polish, soap, hairspray and very often in perfumes. Dimethyl phthalate or DEP are for example added to perfume to slow the rate of evaporation of the aroma. In contrast, a small addition of di-n-butyl phthalate (DBP) is sufficient to confer greater resistance to abrasion and chipping upon nail polish. In contrast, the phthalates containing long alkyl chains, like di(2-ethylhexyl)

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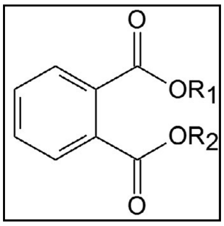

Fig. 1. Chemical structure of phthalic acid esters (where R_1 and R_2 are groups derived from alcohols that may be the same or different alkyl or aryl groups).

phthalate (DEHP), diisononyl phthalate, and butylbenzyl phthalate, gain widespread use as plasticizers in the plastics industry [4], partly on account of the combination of low melting point and high boiling point that also encourages a role as fluids in heat exchangers. The plasticizers referred to are also added to paints and solvents and – as the name suggests – they confer flexibility on materials (e.g. polyvinyl chloride), though also transparency and durability. The efficacy of this action combines with low cost to ensure that plasticizing phthalates are also used in children's toys, while the specific physicochemical properties ensure application in the manufacture of plastic films and sheets, including for the packaging of food.

Yet a further application of phthalates is as components in laboratory products (test tubes, capsules, sept and gloves), and as industrial solvents [5,6].

For all these reasons, production of phthalates grew steadily, reaching 1.9 Mt in 1975, 6.2 Mt in 2009 and >8 Mt in 2011 [7]. While more than 1,200 phthalates are known in total, only 50–100 are of commercial significance, inter alia gaining use in the production of almost 60 different polymers and 30 product groups [8,9].

2. Occurrence of phthalates in the environment

The downside of the wide range of common uses of phthalates (see Table 2) is their release into the environment, which inter alia occurs by migration from for example, plastic, into a carrier with which that plastic is in contact [4]. Such migration into various components of the environment takes place at the production, distribution, use, reuse and storage phases. Typical circumstances involve leaching from plastics and waste into water, arrival in the air and then water following the incineration of plastic waste, or volatilization from polymers [10,11]. The degree of such migration depends on many factors, though primarily on properties of the polymer, types, and amounts of phthalate in use, temperature, and medium [12]. At the chemical level, ease of migration reflects the fact that phthalates are only linked physically, not via chemical linkages into polymer chains.

Once present in the environment, the substances might undergo photodegradation or hydrolysis, but the rates of these processes in natural conditions are found to be low, while the metabolites arising may prove even more toxic than their precursors. Both phthalates and metabolites are to be found in the different phases and components of the environment, including air, surface waters and groundwater, drinking water, bottom sediments of bodies of water, raw and treated sewage, sewage sludge, landfill leachate and even living organisms [7,13–15].

The three main sources of phthalates passing into aquatic ecosystems are considered to be atmospheric precipitation, treated effluent discharged from industrial and municipal wastewater treatment plants, and landfill leachate [14,16–19]. While typical surface waters will have between 0 and even 197 μg/L of these compounds (Table 3), reports in the literature frequently attest to much higher concentrations of these pollutants being present. For example, DEHP was found to be present in German surface waters at 2,700 μg/L [20], while a situation reported in Italy involved 4,600 μg/L [21]. It is DEHP and DBP that tend to be present at highest concentrations, in-line with their being produced in the greatest amounts and made subject to widespread use, as well as the fact that they are degradation-resistant.

Numerous studies also confirm the presence of phthalates in groundwater. Table 4 shows the minimum and maximum concentrations of the four main phthalates observed in groundwater in different countries. High levels reflect leachate from landfills reaching sources of groundwater. Septic-tank and sewer leakage may also have an impact, as phthalates are also released in urine [28].

Table 1
Characteristics of selected phthalates in common use [3,4]

Phthalate	Abbreviation	Chemical formula	Molar mass (g/mol)	Number of carbon atoms in the alkyl chain	Solubility in water at 25°C (g/dm^3)	Log K_{OW}
Dimethyl phthalate	DMP	$C_{10}H_{10}O_4$	194.2	1	<0.100	1.64
Diethyl phthalate	DEP	$C_{12}H_{14}O_4$	222.2	2	1	2.70
Di-n-butyl phthalate	DBP	$C_{16}H_{22}O_4$	278.3	4	0.015	4.83
Diisobutyl phthalate	DIBP	$C_{16}H_{22}O_4$	278.3	4	0.011	4.46
Butyl benzyl phthalate	BBP	$C_{19}H_{20}O_4$	312.4	4 and 6	<0.002	5
Di-n-octyl phthalate	DNOP	$C_{24}H_{38}O_4$	390.6	8	<0.001	7.73
Di(2-ethylhexyl) phthalate	DEHP	$C_{24}H_{38}O_4$	390.6	8	<0.001	8.71
Diisononyl phthalate	DINP	$C_{26}H_{42}O_4$	418.6	9	<0.001	8.60
Diisodecyl phthalate	DIDP	$C_{28}H_{46}O_4$	446.7	10	<0.001	10.47

Table 2
Application of selected phthalates [6]

Phthalate	Application
DEHP	Medical tubes containing polyvinyl chloride, blood bags, medical devices, food packaging, plastic toys, wallpapers, tablecloths, floor tiles, furniture upholstery, shower curtains, garden hoses, inserts for swimming pools, rainwear, children's clothing, dolls and some toys, shoes, car upholstery, foils, and packaging sheets
DEP and DBP	Nail polishes, deodorants, perfumes, pharmaceuticals, insecticides
DNOP	Toys
BBP	Vinyl floors, adhesives, sealants, food packaging, upholstery, vinyl tiles, carpet tiles, and artificial leather
DMP	Insecticides, glues, hair styling products, shampoos, aftershaves

Table 3
Example concentrations of selected phthalates in surface water (μg/L)

River/country	DMP	DEP	BBP	DBP	DEHP	DNOP	Literature
Sungari/China	1–4.1	1.3–6.7	0–4.39	1.69–11.8	2.3–11.6	0.7–6.1	[22]
Port East London/South Africa	0.03–32	0.03–33.1	–	2.8–122	0.06–197	–	[23]
Somma/France	0.02–0.25	0.26–7	–	0.22–3.9	5.16	20.8	[24]
Netherlands	–	0.07–2.3	0.01–1.8	0.01–0.3	0.9–5	–	[25]
15 rivers/France-Belgium	ΣDMP + DEP + BBP + DBP + DEHP + DNOP = 17.20–179						[26]
Yangtze River/China	ΣDMP + DEP + DBP + DEHP + DNOP = 152–450						[27]

– not detected

Table 4
Example concentrations of selected phthalates in groundwater (ng/L)

Country	DEP	BBP	DBP	DEHP	Literature
United Kingdom	1–430	–	99–4,300	50–840	[29]
Japan	–	–	20–350	1,000–18,400	[30]
Europe	100–200	40–240	120–460	70–1,400	
USA	870–1,47,000	0–38	500–50,000	0–470	

– not detected

Despite the aforementioned tendency to migrate, phthalates are only water-soluble to limited extent. They therefore tend to become adsorbed on suspended solids, with the result that they ultimately accumulate in bottom sediments [20,31]. The contents of individual phthalates reported from bottom sediments at selected sites were in the range 0 to even 34.8 mg/kg DW (Table 5). In addition, research conducted in a Chinese city revealed the presence of 16 phthalates in all water samples and reservoir sediments [32].

The accumulation of phthalates in natural waters results in their becoming further distributed across water systems [4]. In Poland and Germany, studies by Luks-Betlej et al. [36] confirmed the presence of DEP, DBP, BBP and DEHP at concentration ranges in water of 0–200, 0–380, 0–50 and 0–60 ng/L respectively. While these values do not exceed acceptable levels, relatively easy penetration of these compounds from various surfaces of everyday materials for food and air makes it necessary to minimize their presence in water. This is especially true given an estimated daily intake of these compounds equal to 7 μg/kg DW [4,37].

Emissions of phthalates from cosmetics, personal care products and plasticizers in the course of the storage process represent an important source of these pollutants in the natural environment. In recent years, high levels of phthalic acid esters have been identified in landfill leachates (Table 6) [38,39]. These results support the view that the level of phthalate-ester pollution is associated with anthropogenic sources. Among the substances detected in the leachate from landfills, it was DEHP, DBP, and di-n-octyl phthalate that were present at highest concentrations – with maxima of 460; 17,900; and 93,300 μg/L respectively [7].

The threat to human and animal health resulting from the wide distribution of phthalates in the environment and everyday objects is the subject of discussion and research by many scientists around the world. The European Union and the US Environmental Protection Agency have identified phthalate esters (DBP, BBP and DEHP) as priority substances, mainly due to their toxicity and resistance to degradation. These compounds also qualify for listing as chemical substances to be screened for the aim being to identify the chemicals, and

Table 5
Example contents of selected phthalates in bottom sediments (μg/kg DW)

Place	DMP	DEP	BBP	DBP	DEHP	DNOP	Literature
Guanting Reservoir, China	0–94.5	0.2–89.5	0–380	0–571	0–278	6.9–258	[33]
Port of Kaohsiung, Taiwan	–	–	–	13–1,331	400–34,800	0–600	[32]
Rivers, Taiwan	–	100–1,100	0–1,800	300–30,300	500–23,900	–	[34]
15 watercourses and rivers, France-Belgium	ΣDMP + DEP + BBP + DBP + DEHP + DNOP = 1,090–11,890						[26]
River Shatt al-Arab, Iraq	ΣDEP + DBP + DEHP + DNOP = 3,800–1,85,100						[35]

– not detected

Table 6
Occurrence of phthalates in leachate from landfills (μg/L)

Place	DMP	DEP	BBP	DBP	DEHP	DNOP	Literature
17 landfills in Europe	–	0–33	0–29	0–7	0–460	–	[40]
Sanitary waste landfill (Brazil)	–	–	17,900	–	–	93,300	[41]
Two landfills in Chennai	–	56.80–495.3	–	–	–	56.80–495.3	[42]
Three landfills in Hubei, China	0–2.80	0–5.7	0.35–59.8	0–21.8	1.61–232.5	0–521.1	[43]
Landfill, Thailand	20.80	12.5	35.4	21.5	65.6	8	[44]

– not detected

their potential impact on the human endocrine system [45]. Of the phthalates mentioned, it is DEHP that is produced in the largest quantities and used in the production of plastic products, hence a confinement to this particular pollutant in the majority of the legal provisions formulated thus far. The World Health Organization (WHO) and the EU have limited the permissible concentration of DEHP in drinking water to 8 μg/L [46]. In turn, the US Safe Water Drinking Act as enforced by the EPA regulates the concentration of DEHP, with a maximum acceptable level in this case of 6 μg/L [47]. Corresponding Australian, Japanese and New Zealand legislation also regulates permissible amounts of DEHP in drinking water, at 9,100 and 10 μg/L respectively [48].

The already-noted fact that DEHP and other phthalates are soluble to only a limited degree ensures that they mainly accumulate on solid particles, including sewage sludge. It is for this reason that the EU has also established an acceptable concentration of phthalates in dehydrated sediments utilizable in agriculture or for natural purposes (this being of 100 mg/kg). Typically, EU rules do not prevent Member States from going further, and Danish law only permits 50 mg of phthalates per kg of dry matter of sediments [49].

The permissible concentration of phthalates in toys is 0.1% about the total weight of the material to which plasticizers are added. Furthermore, the presence of the compounds at concentrations above this is deemed to pose a danger to children – hence regular inspection and monitoring of the toy market. In the years 2013–2017, by virtue of the Trade Inspection Act, the President of Poland's Office of Competition and Consumer Protection (UOKiK) pursued administrative proceedings that culminated in the issue of a total of no fewer than 142 prescriptive orders regarding toys containing phthalates, resulting in the elimination of over 74.500 toy items from the market [50]. The EU also took the initiative and prohibited the use of any phthalates whatever in products designated for children under the age of 3 y. A similar ban on the use of phthalates in toys has also been imposed in California [51].

In turn, in several countries, the place of phthalate DEHP in manufacturing has been taken by others (like diisononyl phthalate (DINP) and IDP), with a view to the health and environmental risks associated with exposure to DEHP being minimized. Unfortunately, this did not prove a good solution, given the results from Frederiksen et al. (2012) [52] regarding a relationship between metabolites of DINP and diisodecyl phthalate and delayed puberty in girls. Long-term exposure to these two phthalates have also been shown to increase blood pressure in both children and adolescents [53].

3. Research aspect

The research aspect presented here concerns concentrations of DEHP detectable in waters (rivers, lakes, and reservoirs) in Poland. As was noted above, DEHP is both the most commonly-used phthalate, and the compound in the group proving most problematic due to its adverse effects on health. It is the only compound of the phthalate group to have been identified as a priority hazardous substance whose quantities in the environment are to be limited. Data on concentrations in the years 2012–2016 derive from all Polish provinces (from Voivodeship Environment Protection Inspectorates), as well as from the Chief Inspectorate for Environmental Protection.

The Ordinance of the Minister of the Environment of 6 May 2016 on the list of priority substances, introduced a listing of one phthalate, that is, DEHP, terming it a priority hazardous substance. In turn, by virtue of the Regulation of the

Minister of the Environment of 21 July 2016 on the method of classifying the status of uniform bodies of surface water and environmental quality standards for priority substances [54], environmental standards have been established. Thus, surface waters are to contain no more than 1.3 μg/L of DEHP. Monitoring of the presence of other substances from the group of phthalic acid esters in the water ecosystem is not carried out.

4. Results

The range of annual average concentrations for DEHP in surface water in Poland are as presented in Fig. 2.

Polish surface waters proved to differ greatly in terms of their contents of DEHP. The range of concentrations was 0–3.22 μg/L, with comparisons in consecutive years not suggesting any intensification of the DEHP pollution problem over time. The DEHP concentration did not exceed the limit values set by WHO and EU in drinking water at the level up to 8 μg/L. Concentrations of the substance appear to have declined in Pomorskie, Warmińsko-Mazurskie and Podlaskie Voivodeships, while remaining the same in waters in other voivodeships. The most severe problem is that facing Podlaskie, where four exceedances were noted in 2012 and 2013. Fig. 3 shows the points at which over concentrations of DEHP above the norm were observed. Exceedances characterized the Rivers Strabelka, Kamianka, Biała, and Horodnianka and reflected respectively concentrations of 1.99, 1.67, 3.22 and 1.78 μg/L. The latest data show the problem in Podlaskie Voivodeship continuing, with an increased concentration of DEHP in surface water (1.14 μg/L). Increased concentrations of DEHP were also found in Pomorskie voivodeship in 2012. In other voivodeships, no exceedances for DEPH was noted, with annual concentrations below the 1.3 μg/L limit value.

A greater degree of contamination with DEHP than was to be noted in other voivodeships may reflect the type of anthropogenic activity, as the quality of water in Podlaskie is the result of accumulated pressure associated with the discharge of municipal and industrial wastewaters, effluent from agricultural activity, areal runoff from agricultural land, rainwater and snowmelt from urban areas, and communal and residential sewage from rural areas. Largest amounts of sewage and greatest discharged loads of pollutants come from the cities in which economic activity and industry are concentrated, and it is the production and processing of foodstuffs that may be of key importance. Podlaskie Voivodeship is a region dominated by agriculture, which accounts for some 60% of its land [55,56]. More specifically, farm production here is dominated by livestock, and by milk production and animal husbandry in particular. Podlaskie comes second in Poland where milk production is concerned, while it is 7th in the ranking of voivodeships for cattle breeding in general. Silage production under plastic sheeting is now widely practised in the latter context, especially where herds are larger and silage is the main kind of fodder. Current technologies for the production of agricultural plastic sheeting, nets and prism film usually entail the manufacture of multilayer films of polyethylene or polypropylene, as softened by phthalates

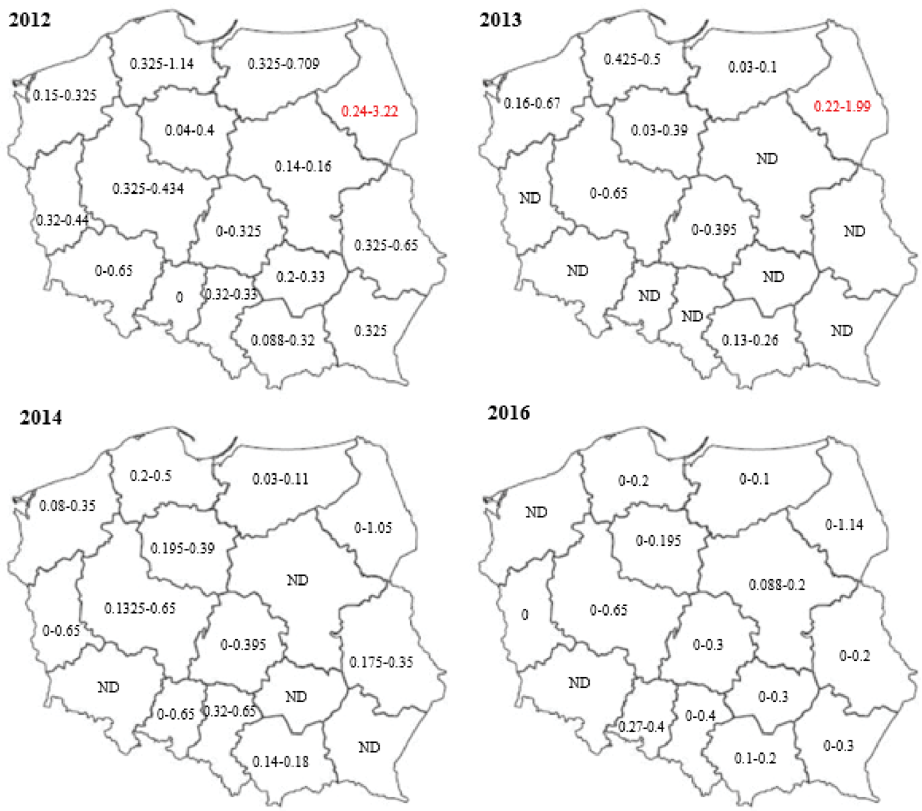

Fig. 2. Range of annual average concentrations for DEHP in different voivodeships and different years.

Fig. 3. Distribution of points at which the permissible concentration of DEHP was exceeded (Podlaskie Voivodeship).

(primarily HDPE). Data for Mazowieckie voivodeship suggest that only 7.02% of 1,297 farms surveyed optimally managed their plastic, by recycling.

Meanwhile, the exposure of wrapped bales to direct solar radiation reduces the durability of plastic significantly, encouraging leaching of the plasticizer and increasing permeability to gases. This ensures that surface runoff of pollutants (also including agricultural chemicals) from farmland has a significant impact on water quality [55–59].

Recent years have been a period of particularly dynamic development of the food industry, thanks to which, in today's Podlaskie, it is large factories that process milk, meat, poultry, and cereals. The dairies here operating based on modern technologies are now among Poland's largest and most modern [56].

Further sources of water pollution in this voivodeship include municipal and industrial wastewater treatment plants. In recent years, there has been a steady reduction in the volume of pollutants discharged into waters. The observed trend is conditioned by several factors, including the collapse of several large state-owned enterprises, a reduction in output and a change in the profile of production. A reduction in the volume of wastewater generated is also very much down to reduced water absorption and modernized production processes, as well as modernization of wastewater treatment plants and an increase in the level of efficiency of treatment processes. In 2014, 100% of municipal and industrial effluent requiring treatment was treated. This was the year in which a decrease in the concentration of DEHP in surface waters to a value below the threshold was also observed [55,56].

Climatic conditions may also affect amounts of DEHP. The Podlaskie region has the most severe climatic conditions of any lowland part of Poland, especially in terms of precipitation and temperature.

The presence of DEHP in waters can also be caused by the manufacture of various types of products containing the compound, from leaching or the improper handling of waste. Poorer water quality in Podlaskie Voivodeship is also the result of pressure relating to water intake, as well as the way in which rainwater and water from melting snow are dealt with [56–60].

The largest exceedances noted for the tested compound occurred in the River Biała, probably on account of it's flowing through Podlaskie's largest city – Białystok. This is also receiving water for both precipitation runoff and treated sewage. In 2012, a serious problem related to fish deaths was noted here. According to the Provincial Environmental Protection Inspectorate in Białystok, the cause could have been an illegal connection or a leak caused by a breakdown. The Kamianka also flows through the areas of two cities, potentially therefore, collecting polluted runoff from industrial areas or sewage. Exceedances along the Horodnianka may, in turn, reflect influxes of hospital wastewater [56,60–62].

Those analyzing the degree of pollution of individual components of the environment with organic compounds should take account of physico-chemical properties determining both place and form of occurrence. Being only slightly water-soluble, DEHP is usually sorbed on solid particles, with sedimentary suspension ensuring accumulation in bottom sediments. This is to say that a reduction in the concentration of the substance in water may reflect further accumulation in sediments. Fig. 4 shows average DEHP contents noted for bottom sediments, about province and year of study.

Assessment of bottom sediment contamination with DEHP is carried out based on ecotoxicological criteria. Since 2013, the assessment of the status of bottom sediment pollution in Poland has been extended to include DEHP. The threshold DEHP content in bottom sediments are shown in Table 7. At present, no monitoring is carried out for the other substances from the phthalic acid ester group.

For the DEHP content, the limit values of level III quality of bottom sediment purity were not exceeded. For such concentration values, there should be no negative effects on benthic organisms. DEHP contents ranged from 0–7.1 mg/kg DW, with the highest value of all being noted in a water in Małopolskie voivodeship in 2014. Unfortunately, data on the level of DEHP in this place in other years are lacking. In contrast, waters in Podlaskie Voivodeship have low DEHP contents in bottom sediments compared with the rest of the country, amounting as they do to 0.1 mg/kg DW. An upward trend for DEHP if to be observed for bottom sediments in waters of Pomorskie and Wielkopolskie voivodeships, while the trend was downwards in Kujawsko-Pomorskie, Warmińsko-Mazurskie, and Zachodniopomorskie. In other regions of the country, there were no significant changes in contents of DEHP in bottom sediments from year to year.

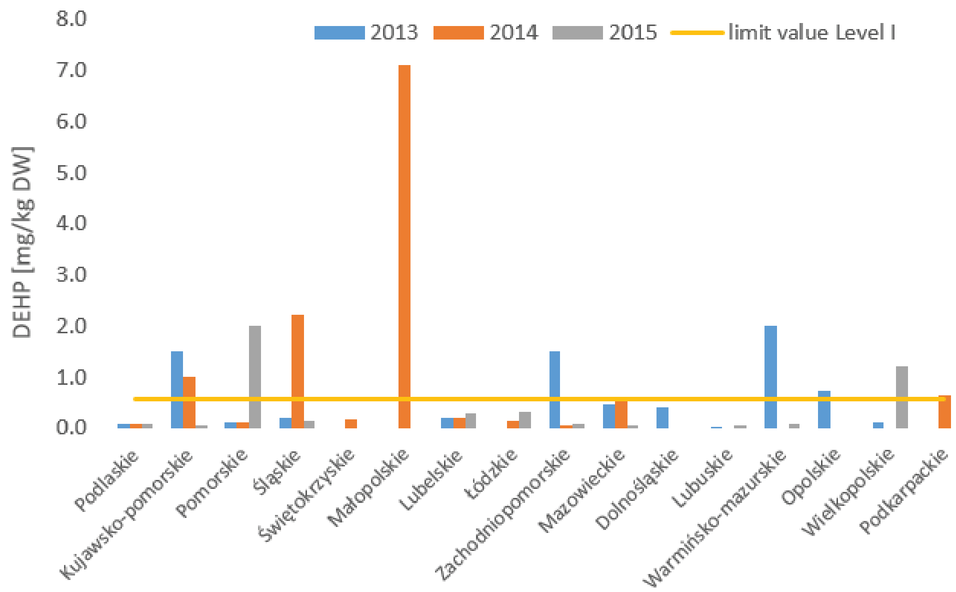

Fig. 4. Highest analyzed contents of DEHP in bottom sediments in different voivodeships of Poland.

Table 7
DEHP threshold content in bottom sediments [55]

Substance	Level I ≤ TEC	Level II > TEC ≤ MEC	Level III > MEC ≤ PEC	Level IV > PEC
	(µg/kg)			
Di(2-ethylhexyl) phthalate	≤580	580–22 790	22 790–45 000	>45 000

TEC – Threshold effect concentration; PEC – Probable effect concentration; MEC – Midpoint effects concentrations

5. Conclusions

The results and data analysis presented in the article indicate the emerging problem of pollution with environmentally hazardous substances from the group of phthalic acid esters. Their presence is detected in each component of the environment in a wide range of concentrations. Their presence mainly results from widespread use as plasticizers. Most often, DEHP is used for these purposes. The permissible concentrations of this substance in surface waters were exceeded by up to 3.22 μg/L in Podlaskie Voivodeship. Analysis of potential sources of DEHP in Podlaskie's surface waters suggests this negative pollution phenomenon is first and foremost linked with means of managing catchments. By virtue of the Regulation of the Minister of the Environment of 21 July 2016 on the method of classifying the status of uniform bodies of surface water and environmental quality standards for priority substances [54], surface waters are to contain no more than 1.3 μg/L of DEHP. However, the DEHP concentration in drinking water up to 8 μg/L set by WHO and EU was not exceeded in any case.

However, due to its physicochemical properties, this substance accumulates in bottom sediments. The DEHP content in bottom sediments reached levels up to 7,100 μg/kg DW. The limit values of level III ecotoxicological criteria were not exceeded. The exceedances noted for DEHP necessitate ongoing monitoring of waters, and above all of their bottom sediments.

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